DESCRIPTION

PLASMA DISPLAY DEVICE

TECHNICAL FIELD

The present invention relates to a plasma display device used for displaying images such as a television receiver and the like.

BACKGROUND ART

Among color display devices used for image display such as computers and televisions, certain display devices equipped with plasma display panels (hereinafter referred to as "PDP" or "panel") are drawing attention in recent years as color display devices for providing large screens while maintaining thin forms and light weights.

PDP presents full color display through the process of mixing the so-called three primary colors (i.e., red, green and blue). In order to make full color display, the PDP is provided with phosphor layers for luminous emission of the three individual primary colors of red (R), green (G) and blue (B), wherein phosphor particles composing the phosphor layers produce visible light of the individual colors when excited by ultraviolet rays generated inside discharge cells of the PDP.

Substances such as (Y, Gd) $BO_3:Eu^{3+}$ and $Y_2O_3:Eu^{3+}$ which emit red light and become charged positively (+), $Zn_2\ SiO_4:Mn^{2+}$ which emits green light and becomes charged negatively (–), $BaMgAl_{10}O_{17}:Eu^{2+}$ which emits blue light and becomes charged positively (+), and the like chemical compounds are used as phosphors of the individual colors, as they are disclosed in "O plus E" (February, 1996, No. 195, pp 99-100) and the like non-patent publications, for instance.

In addition, "Phosphor Handbook" (Ohmsha, Ltd., pages 219 and 225) and other non-patent publications disclose a technique in which each of these phosphors is made by the process of mixing certain raw materials and firing them at a temperature of 1000 deg-C or higher to cause a solid phase reaction.

In a combination of the conventional phosphors of red, green and blue colors, only the green phosphor is charged negative, and this tends to cause discharge failures because an amount of electric charge carried in the green phosphor differs greatly as compared to those of the red and blue colors. Therefore, another technique is disclosed in Japanese Patent Unexamined Publication, No. 2001-236893, in which YBO_3:Tb having positive charge (+) is mixed with Zn_2SiO_4:Mn to bring the amount of electric charge as close as possible to those of the red and blue colors, and to avoid discharge failures. There is also another technique disclosed in Japanese Patent Unexamined Publication, No. 2003-7215, in which a discharging characteristic and brightness degradation are improved by using a mixture of $BaAl_{12}O_{19}$:Mn or $BaMgAl_{14}O_{23}$:Mn having a positive charge (+) and (Y, Gd) BO_3:Tb or $LaPO_4$:Tb, also having a positive charge (+).

However, there exists a problem with the green phosphor as described below, when producing a PDP of high brightness by increasing a density of Xe gas inside the PDP with any mixture of the prior art phosphor materials.

A panel made of $BaMgAl_{10}O_{17}$:Eu for the blue color, Zn_2SiO_4:Mn for the green color and a mixture of (Y, Gd) BO_3:Eu and Y_2O_3:Eu for the red color carries positive charges (+) on the surfaces of the blue phosphor and the red phosphor among all these phosphors. However, since the green phosphor made of Zn_2SiO_4:Mn has a larger ratio of SiO_2 in proportion to ZnO (i.e., 1.5·ZnO/SiO_2) than a stoichiometric ratio (2·ZnO/SiO_2) for the reason attributed to manufacturing of the phosphor, a surface of Zn_2SiO_4:Mn crystal is covered with SiO_2, and the

phosphor surface is thus charged negative (–). In the PDP having both the phosphors charged negative (–) and positive (+) in coexistence, there generally is a problem that the negative charge remains only on the negatively charged phosphor, especially when the entire screen is put out after having been lit into a full luminance while the panel is driven, and this causes discharge failures such as instability and absence of discharge when the voltage is impressed for the subsequent image display. It has been found that these problems become exceptionally noticeable when the amount of Xe in the discharge gases is increased to 5% or more in an attempt to improve the brightness and efficiency of the PDP.

Furthermore, Zn_2SiO_4:Mn used for the green color remains in such a state that it is very liable to adsorb gases, especially because its surface is covered with SiO_2. In other words, Zn_2SiO_4:Mn has adsorbed a large amount of moisture (H_2O), carbon monoxide (CO), carbon dioxide (CO_2), and/or hydrocarbon gases (C_xH_y) left as byproducts of the decomposed organic binder. They are gasified and released inside the panel during the aging process after the panel is sealed, and they result in degradation of the discharging characteristic when they are adsorbed in the surface of MgO. Moreover, these gases are adsorbed in the surfaces of the blue color phosphor of $BaMgAl_{10}O_{17}$:Eu and the green color phosphor of Zn_2SiO_4:Mn, and cause surface reactions. As a result, there is a problem that brightness decreases and a y-value of chromaticity rises in the blue color, thereby decreasing a color temperature and causing blur in color of the panel.

On the other hand, there is a panel so contrived as to have a combination of green phosphors composed of Zn_2SiO_4:Mn having a surface of negative charge and $ReBO_3$:Tb ("Re" represents a rare earth element such as Sc, Y, La, Ce and Gd) having a surface of positive charge, which are mixed in a manner that they

are charged virtually positive (+), blue phosphor of $BaMgAl_{10}O_{17}$:Eu and red phosphor of (Y, Gd) BO_3:Eu, both having positive charges. In the panel of this example, although there is an improvement to some extent of the discharge failures due to unbalance of the electric charges, it still increases the discharge failures when the density of Xe gas is raised.

In addition, this example causes deterioration of MgO due to H_2O, CO, CO_2 and C_xH_y gases released inside the panel during discharging operation as described above, and lowers the discharging characteristic including variations and failures of the discharge, since it contains Zn_2SiO_4 which is liable to adsorb H_2O and C_xH_y gases. It also has a problem of degrading the brightness and causing blur in the color attributable to surface reaction of these gases with the phosphors of $BaMgAl_{10}O_{17}$:Eu and Zn_2SiO_4:Mn.

The discharge failures can be prevented to some extent if all the phosphors are composed of the materials having positive charges (+), such that the panel employs a combination of green phosphor made of a mixture of any of $BaAl_{12}O_{17}$:Mn, $BaMgAl_{10}O_{17}$:Mn, (Y, Gd) BO_3:Tb and $LaPO_4$:Tb, all having positive charges (+), in place of the Zn_2SiO_4 of negative charge (–), blue phosphor of $BaMgAl_{10}O_{17}$:Eu, and red phosphor of any of (Y, Gd) BO_3:Eu and Y_2O_3:Eu.

However, this gives rise to another problem that failures and variations of discharge increase since the discharge voltage rises if the amount of Xe in the discharge gases exceeds 5% (or, especially when it exceeds 10%). Besides the degradation of these discharge characteristics, $BaAl_{12}O_{19}$:Mn and $BaMgAl_{14}O_{23}$:Mn, in particular, contain many defects within their crystal structures among the above green phosphors, and they are therefore liable to adsorb H_2O and C_xH_y gases. In addition, $LaPO_4$:Tb is also liable to adsorb H_2O and hydrocarbon (C_xH_y) gases because it contains PO_4 in the crystal structure.

For this reason, H_2O and C_xH_y gases are released inside the panel during the aging process, and these gases cause chemical reactions over the surfaces of the phosphors, thereby accelerating degradation of the brightness during an extended period of lighting operation of the panel. Degradation of the brightness in the blue and green colors lowers a color temperature when the panel is lit for the full-on white screen, and this gives rise to still another problem in which the color of the panel blurs so that the screen becomes yellowish.

The present invention was contrived in consideration of the above problems, and it is an object of this invention to provide a plasma display device comprised of a green phosphor which is charged entirely with a positive potential (+), lessens adsorption of H_2O, CO, CO_2 and C_xH_y gases, and reduces chemical reactions to them.

SUMMARY OF THE INVENTION

In order to achieve the above object, the present invention provides a green phosphor layer formed of a green color phosphor comprising at least one kind of chemical compound selected from among those given by general formulae of M_{1-a} $(Ga_{1-x}Al_x)_2$ O_4:Mn_a (where "M" denotes one of Zn, Mg, Ca and Sr), $(Y_{1-a-y}Gd_a)$ $(Ga_{1-x}Al_x)_3$ $(BO_3)_4$:Tb_y, $(Y_{1-a-y}Gd_a)$ $(Ga_{1-x}Al_x)_3$ $(BO_3)_4$:Ce_y, Tb_y, $(Y_{1-a-y}Gd_a)$ BO_3:Tb_y and $(Y_{1-a-y}Gd_a)_3$ $(Ga_{1-x}Al_x)_5$ O_{12}:Tb_y.

In other words, the green phosphor used here as the chemical compound featuring high brightness, carrying positive charge (+) and not being liable to react with water and hydrocarbon gases is one of or any combination of two or more kinds of phosphors selected from among $Zn(Ga_{1-x}Al_x)_2$ O_4:Mn, $Mg(Ga_{1-x}Al_x)_2$ O_4:Mn, $Ca(Ga_{1-x}Al_x)_2$ O_4:Mn, $Sr(Ga_{1-x}Al_x)_2$ O_4:Mn, (Y, Gd) $(Ga_{1-x}Al_x)_3$ $(BO_3)_4$:Tb, (Y, Gd) BO_3:Tb, (Y, Gd) $(Ga_{1-x}Al_x)_3$ $(BO_3)_4$:Ce, Tb, Y_3

$(Ga_{1-x}Al_x)_5O_{12}$:Tb and $ZnAl_2O_4$:Mn.

According to the above composition, amounts of electric charges carried on the red, green and blue phosphors become generally equal since all the phosphors are charged with positive potential (+), and this practically eliminates variation of discharges among the red, green and blue phosphors during address discharge, thereby avoiding discharge failures. In addition, these green phosphors are made of materials having high coefficient of electron emission, such as Al and Y, and comprised of the host material of oxide compounds featuring low absorption of water and hydrocarbon gases. They therefore do not cause significant increase in the discharge voltage even if the panel contains 5% or more in the amount of Xe gas, and they can further reduce discharge failures without increasing the voltage for address discharge even when a partial pressure of the Xe gas is raised.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a plan view depicting a PDP for use in a plasma display device with a front glass substrate removed, according to an exemplary embodiment of the present invention;

Fig. 2 is a perspective view depicting a structure of an image display area of the PDP;

Fig. 3 is a block diagram of the plasma display device according to the exemplary embodiment of this invention;

Fig. 4 is a cross sectional view depicting the structure of the image display area of the PDP for use in the plasma display device according to the exemplary embodiment of this invention; and

Fig. 5 is a schematic illustration of an ink application apparatus used for forming phosphor layers of the PDP.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Description will be provided hereinafter of a plasma display device according to an exemplary embodiment of the present invention with reference to the accompanying drawings.

Fig. 1 is a plan view depicting a PDP used for the plasma display device with its front glass substrate removed, according to this exemplary embodiment of the invention, and Fig. 2 is a perspective view depicting a structure of an image display area of the PDP. In Fig. 1, some of electrodes among groups of display electrodes, display scan electrodes and address electrodes are intentionally not shown in order to make them simple and intelligible.

As shown in Fig. 1, PDP 100 comprises front glass substrate 101 and rear glass substrate 102. Front glass substrate 101 has "N" rows each of display electrodes 103 and display scan electrodes 104 formed thereon, and rear glass substrate 102 has "M" columns of address electrodes 107 formed thereon (where "N" represents an integral number indicating a sequential position of the row, and "M" represents another integral number, indicating a sequential position of the column). Front glass substrate 101 and rear glass substrate 102 are sealed with hermetic seal layer 121 shown by slant lines. Individual electrodes 103, 104 and 107 compose a triple-electrode matrix structure, and cells are formed at intersections between display scan electrodes 104 and address electrodes 107. Front glass substrate 101 and rear glass substrate 102 form discharge space 122 between them to provide display area 123.

This PDP 100 has a structure, as shown in Fig. 2, which comprises a front panel provided with display electrodes 103, display scan electrodes 104, dielectric glass layer 105 and MgO protective layer 106 on a major surface of front glass substrate 101, a rear panel provided with address electrodes 107,

dielectric glass layer 108, barrier ribs 109, phosphor layers 110R, 110G and 110B on a major surface of rear glass substrate 102, and discharge gases filled inside discharge space 122 formed between the sealed front and rear panels. PDP 100 is connected with PDP drive unit 150 shown in Fig. 3, to complete the plasma display device.

The individual electrodes of PDP 100 are connected with display driver circuit 153, display scan driver circuit 154 and address driver circuit 155, as shown in Fig. 3, to operate the plasma display device. A voltage is applied between display scan electrode 104 and address electrode 107 to initiate an address discharge in a cell where luminous emission is to be made, under the operation of controller 152. Following the above, a pulse voltage is applied between display electrode 103 and display scan electrode 104 to obtain a self-sustained discharge. The self-sustained discharge generates ultraviolet rays in the cell, which in turn excite the phosphor layer to illuminate and light the cell. A visual image is hence displayed by on-and-off combinations of the individual cells of different colors.

Description is provided next of a method of manufacturing PDP 100 discussed above.

The front panel is constructed in a manner that "N" rows each of display electrodes 103 and display scan electrodes 104 are formed alternately in parallel to each other in a striped pattern on front glass substrate 101 (Fig. 2 shows only two rows each of them), the electrodes are then covered with dielectric glass layer 105, and MgO protective layer 106 is additionally formed on the surface of dielectric glass layer 105. Display electrodes 103 and display scan electrodes 104 are made of silver, and they are formed by coating a silver paste suitable for the electrodes with a screen printing method, and by firing them thereafter.

Dielectric glass layer 105 is formed into a predetermined thickness (approx. 20μm) by coating a paste containing lead-oxide base or zinc-oxide base glass material using a screen printing method, followed by firing at a predetermined temperature for a predetermined time, for instance, at 560 deg-C for 20 minutes. An example of materials suitable for the paste containing lead base glass material is a compound of PbO (70wt%), B_2O_3 (15wt%), SiO_2 (10wt%) and Al_2O_3 (5wt%) mixed in an organic binder (e.g., a solution of 10% ethyl cellulose in α-terpineol). The organic binder in this embodiment is a substance produced by dissolving a polymeric resin into organic solvent, and that other materials may also be used such as acrylic resin instead of ethyl cellulose as the resin material, and butyl-carbitol as the organic solvent. In addition, the organic binder may also be mixed with a dispersing agent such as glyceryl trioleate.

MgO protective layer 106 is made of magnesium oxide (MgO), and it is formed into a prescribed thickness (approx. 0.5μm) by a sputtering method or a CVD method (i.e., chemical vapor deposition) for example.

The rear panel is constructed in a manner that "M" columns of address electrodes 107 are formed into a striped pattern on rear glass substrate 102, first by printing a silver paste suitable for the electrodes, and firing them thereafter. Dielectric glass layer 108 is formed over address electrodes 107 by coating a paste containing lead oxide base or zinc oxide base glass material using the screen printing method. In the like manner, barrier ribs 109 are formed by depositing a photosensitive paste containing lead oxide base or zinc oxide base glass material repeatedly at predetermined intervals by using the screen printing method, and firing them thereafter. These barrier ribs 109 divide discharge space 122 into a number of individual cells (unitary emissive areas) in one linear direction.

Fig. 4 is a cross sectional view of PDP 100. Dimension "W" of the spaces

formed by barrier ribs 109, as shown in Fig. 4, is fixed to a given value, or approx. 130μm to 240μm, for example in the case of high-definition TV of 32 to 50 inch size. Inside the grooves between barrier ribs 109, there are phosphor layers formed of a red phosphor of yttrium oxide group as red phosphor layers 110R, of which surfaces are charged positive (+), as well as phosphor layers formed of a blue phosphor having a β-alumina crystal structure as blue phosphor layers 110B, of which surfaces are also charged positive (+). There are also green phosphor layers 110G formed of a green phosphor comprising at least one or a combination of any materials selected from among spinel group compounds of $M(Ga_{1-x}Al_x)_2\,O_4{:}Mn$ (where "M" denotes one of Zn, Mg, Ca and Sr) containing aluminum, of which surfaces are charged negative (+), and aluminate group compounds of $(Y_{1-x}Gd_x)\,BO_3{:}Tb$, $(Y_{1-x}Gd_x)\,(Ga_{1-x}Al_x)_3\,(BO_3)_4{:}Tb$, $(Y_{1-x}Gd_x)\,(Ga_{1-x}Al_x)_3\,(BO_3)_4{:}Ce$, Tb, and $(Y_{1-a-y}Gd_a)_3\,(Ga_{1-x}Al_x)_5\,O_{12}{:}Tb_y$ containing yttria, of which surfaces are also charged positive (+). These phosphor layers 110R, 110G and 110B are formed of phosphor inks of the individual colors made of color phosphor particles dissolved with organic binder into paste form, which are deposited on the inner surfaces of the barrier ribs, and fired at a temperature of approximately 500 deg-C to burn off the organic binder and to firmly bind together the color phosphor particles. It is desirable to form these phosphor layers 110R, 110G and 110B so that thicknesses "L" of the layers deposited above address electrodes 107 becomes approximately 8 to 25 times the mean diameter of the phosphor particles of individual colors. In other words, it is desirable for the phosphor layers to have a thickness equal to at least 8 layers and preferably about 20 layers of the phosphor particles in order to ensure a sufficient brightness (i.e., emission efficiency) when ultraviolet rays of a given intensity are irradiated to these phosphor layers. This is because any thickness greater than the above value results in a virtual

saturation of the emission efficiency of the phosphor layers, and deprives discharge spaces 122 of sufficient size.

The front panel and the rear panel produced as described above are placed together in a manner that the individual electrodes on the front panel cross at right angles with the address electrodes on the rear panel, and they are hermetically sealed by putting sealing frit throughout the perimeter of the panels and firing it at about 450 deg-C for 15 minutes to form hermetic seal layer 121. After that, the interior of discharge space 122 is evacuated to a high vacuum of 1.1×10^{-4} Pa, for instance, and filled with discharge gas comprising a mixture of inert gases such as He-Xe group, Ne-Xe group, He-Ne-Xe group and Ne-Kr-Xe group gases to a predetermined pressure (i.e., 50 to 80kPa) with 5% or more in the partial pressure of Xe. PDP 100 is thus manufactured. This panel is completed after being subjected to an aging process for 5 hours under the conditions of 175V in discharge voltage and 200kHz in discharge frequency.

Fig. 5 is a schematic illustration of ink application apparatus 200 used for forming phosphor layers 110R, 110G and 110B. Ink application apparatus 200 comprises server 210, pressure pump 220 and header 230, as shown in Fig. 5, wherein phosphor ink stored in and supplied from server 210 is pressurized by pressure pump 220 and delivered to header 230. Header 230 has ink chamber 230a and nozzle 240, and it is so constructed that the pressurized phosphor ink delivered to ink chamber 230a is ejected continuously from nozzle 240. Aperture diameter "D" of nozzle 240 needs to be at least 30μm to prevent it from being clogged, and it is normally designed to be 30 to 130μm, which is equal to or smaller than dimension "W" (approx. 130μm to 200μm) of the spaces between barrier ribs 109, so as to prevent the phosphor ink from flowing over the barrier ribs 109 during application.

Header 230 is driven linearly by a header scanning mechanism, which is not

shown in the figure, in such a manner that it continuously ejects phosphor ink 250 from nozzle 240 while being scanned, so that phosphor ink 250 is deposited uniformly throughout the grooves between barrier ribs 109 on rear glass substrate 102. The phosphor ink used here has its viscosity kept within a range of 1,500 to 50,000CP at 25 deg-C.

The above server 210 is equipped with a stirring apparatus, though not shown in the figure. The stirring apparatus prevents fine particles in the phosphor ink from precipitating. Header 230 is constructed integrally with ink chamber 230a and nozzle portion 240, and it is made of a metallic material by machining and fabrication with electrical discharge.

The method of forming the phosphor layers is not limited to the one discussed above, but many other methods can be used such as the photolithography, screen printing, a method of disposing a film containing mixture of phosphor particles, and the like.

The phosphor ink is the mixture of phosphor particles of each color with a binder and solvent, so prepared as to become 1,500 to 50,000 centipoise (CP). It may be added with a surface active agent, silica, dispersing agent (0.1 to 5 wt-%) and the like ingredients if necessary.

The red phosphor used for the mixture of this phosphor ink is one of chemical compounds defined as $(Y, Gd)_{1-x}BO_3{:}Eu_x$ and $Y_{2-x}O_3{:}Eu_x$. They are such compounds in which a part of Y element ("yttrium") composing the host material is substituted by Eu ("europium"). It is desirable here that substituted value X of the Eu element for the Y element is arranged to be in a range of $0.05 \leq X \leq 0.20$. Any substituted value greater than that is considered not practically useful since it substantially accelerates degradation of the brightness although it initially increases the brightness. On the other hand, any value less than that is considered too low a composite ratio of Eu as the

basic element of luminescence, and it becomes not suitable for the phosphor material because of low brightness.

A material used as the green phosphor is any of spinel group compounds defined as M_{1-a} $(Ga_{1-x}Al_x)_2$ O_4:Mn_a (where "M" denotes one of Zn, Mg, Ca and Sr, and desirable ranges of "a" and "x" are $0.01 \le a \le 0.06$ and $0.1 \le x \le 1.0$ respectively) and yttria group compounds $(Y_{1-a-y}Gd_a)$ BO_3:Tb_y, $(Y_{1-a-y}Gd_a)$ $(Ga_{1-x}Al_x)_3$ $(BO_3)_4$:Tb_y, $(Y_{1-a-y}Gd_a)$ $(Ga_{1-x}Al_x)_3$ $(BO_3)_4$:Ce_y, Tb_y and Y_3 $(Ga_{1-x}Al_x)_5$ O_{12}:Tb, and a mixture of some of the above phosphors, all of which surfaces are charged positive (+).

It is desirable here that substituted value "x" of Al for Ga, substituted value "a" of Gd for Y, and another substituted value "y" of Tb for Y are arranged to be within ranges of $0.1 \le x \le 1.0$, $0 \le a \le 1$ and $0.02 \le y \le 0.4$ respectively.

A material used as the blue phosphor is any of chemical compounds defined as Ba_{1-x} Mg Al_{10} O_{17}:Eu_x and Ba_{1-x-y} Sr_y Mg Al_{10} O_{17}:Eu_x. Both Ba_{1-x} Mg Al_{10} O_{17}:Eu_x and Ba_{1-x-y} Sr_y Mg Al_{10} O_{17}:Eu_x are such compounds in which a part of Ba element composing the host material is substituted by Eu or Sr. It is desirable here that substituted value "x" of the Eu element for the Ba element and another substituted value "y" of the Sr element are within ranges of $0.03 \le x \le 0.2$ and $0.1 \le y \le 0.5$ respectively.

A method of synthesizing these phosphors will be described later. The binder to be mixed with the phosphor ink may be ethyl cellulose or acrylic resin (0.1 to 10 wt-% of the ink is mixed), and the solvent used for it can be α-terpineol or butyl-carbitol. Alternatively, polymers such as PMA and PVA may be used as the binder, and diethylene glycol and methylic ether may be used as the solvent.

In this exemplary embodiment, the phosphor particles used are manufactured by using any of solid phase firing method, aqueous solution

method, atomized firing method and hydrothermal synthesizing method. Description is provided next of these methods of manufacturing the phosphor particles.

Described first pertains to the blue phosphor.

To start with, teaching is given of the blue phosphor of $Ba_{1-x}MgAl_{10}O_{17}:Eu_x$.

In the process of making a mixed solution, raw materials of barium nitrate, $Ba(NO_3)_2$, magnesium nitrate, $Mg(NO_3)_2$, aluminum nitrate, $Al(NO_3)_3$ and europium nitrate, $Eu(NO_3)_2$, are mixed to a mole ratio of 1−X:1:10:X (where $0.03 \leq X \leq 0.25$), and this mixture is dissolved in an aqueous medium to prepare a hydrated solution. Ion exchanged water and pure water are desirable for the aqueous medium because they do not contain impurities. However, any such water containing nonaqueous solvent (e.g., methanol, ethanol and the like) may still be useable.

Next, the hydrated solution is poured into a container made of a non-corrosive heat resistant material such as gold or platinum, and subjected to a hydrothermal synthesis (for 12 to 20 hours) under a predetermined temperature (100 to 300 deg-C) and a predetermined pressure (0.2 to 10MPa) in a pressurized vessel by using an apparatus capable of heating while pressurizing such as an autoclave, to synthesize the phosphor particles.

The fine particles are then fired at a predetermined temperature for a predetermined time (e.g., at 1,350 deg-C for 2 hours) in a reducing atmosphere (e.g., in an ambience containing 5% hydrogen and 95% nitrogen), and the produced particles are classified to obtain the desired blue phosphor of $Ba_{1-x}MgAl_{10}O_{17}:Eu_x$. Next, the particles are annealed at 700 to 1,000 deg-C in an oxygen and nitrogen atmosphere to transform a part of bivalent Eu into trivalent Eu, in order to remove oxygen defects and to reduce their surfaces that adsorb water and hydrocarbon gases.

The blue phosphor can also be made by the spray atomizing method in which the phosphor is synthesized by spraying the above hydrated solution into a high temperature furnace through a nozzle.

Description is provided next of the blue phosphor of Ba_{1-x-y} Sr_y Mg Al_{10} O_{17}:Eu_x.

This phosphor is made by the solid phase reaction method in the same manner as the above Ba_{1-x} Mg Al_{10} O_{17}:Eu_x, but only from different raw materials. Details of the raw materials used are described hereafter. The raw materials of barium hydroxide, $Ba(OH)_2$, strontium hydroxide, $Sr(OH)_2$, magnesium hydroxide, $Mg(OH)_2$, aluminum hydroxide, $Al(OH)_3$ and europium hydroxide, $Eu(OH)_2$, are weighed to the required mole ratio. These materials are mixed together with flux of AlF_3, and fired at a predetermined temperature (1,300 to 1,400 deg-C) for a predetermined time (12 to 20 hours) to obtain phosphor particles of Ba_{1-x-y} Sr_y Mg Al_{10} O_{17}:Eu_x in which Mg and Al are substituted by tetravalent ions. This method can produce the phosphor particles having a mean particle diameter of approx. 0.1 to 3.0μm.

The phosphor particles are then fired at 1,000 to 1,600 deg-C for 2 hours in a reducing atmosphere containing 5% hydrogen and 95% nitrogen, for instance, and the produce is classified by using an air classifier to obtain fine phosphor particles. Finally, the particles are annealed at 700 to 1,000 deg-C in an oxygen and nitrogen atmosphere to transform a part of bivalent Eu to trivalent Eu, in order to remove oxygen defects and to reduce their surfaces that adsorb water and hydrocarbon gases.

Although oxide compounds, nitrate compounds and hydroxide compounds are used mainly as the raw materials of the above phosphors, like phosphor can be produced by using organometallic compounds containing Ba, Sr, Mg, Al, Eu and the like, such as metal-alkoxide and acetylacetone.

Described next pertains to the green phosphors of M $(Ga_{1-x} Al_x)_2 O_4$:Mn and $(Y_{1-x} Gd_x) Al_3 (BO_3)_4$:Tb.

To start with, description is given of the spinel group phosphor of M $(Ga_{1-x} Al_x)_2 O_4$:Mn. Since the luminous material Mn is substituted by element M (which represents one of Zn, Mg, Ca and Sr), this compound is expressed by the chemical formula of $(M_{1-a} Mn_a) (Ga_{1-x} Al_x)_2 O_4$.

An example is given here for the case wherein M represents Zn. Zinc oxide, ZnO, gallium oxide, Ga_2O_3, aluminum oxide, Al_2O_3 as the raw materials used for making the phosphor by the solid phase process, and manganese carbonate, MnO_2 as the luminous material are combined according to the required mole ratio of the oxide compounds and predetermined "a" and "x" values, in a manner so that their composite becomes $(Zn_{1-a} Mn_a) (Ga_{1-x} Al_x)_2 O_4$. The combined materials are then mixed with a small amount of flux (AlF_3 and NH_4F). Next, the mixture is fired at a temperature of 950 to 1,300 deg-C for 2 hours in an air ambient. The phosphor can also be produced in the same manner as above when the element M is any of Mg, Ca and Sr. After the produce is crushed lightly to an extent that cohered lumps are loosened, it is fired at 900 to 1,200 deg-C in an nitrogen atmosphere or nitrogen and hydrogen atmosphere,. The produced particles are pulverized, and annealed at 500 to 900 deg-C in an oxygen atmosphere or oxygen and nitrogen atmosphere in order to remove oxygen defects and to reduce their surfaces that adsorb water and hydrocarbon gases. The green phosphor which is charged positive is hence produced.

When producing yttrium group green phosphor, raw materials of yttrium oxide (Y_2O_3), gadolinium oxide (Gd_2O_3), gallium oxide (Ga_2O_3), aluminum oxide (Al_2O_3), boron oxide (B_2O_3) and the luminous material of terbium oxide (Tb_2O_3) are combined according to the composite ratios of the phosphor in the like manner as the spinel group phosphor, and the combined material is fired at a

temperature of 900 to 1,300 deg-C for 4 hours in an air ambient after having mixed with a small amount of flux. Next, after the produce is crushed lightly to an extent that cohered lumps are loosened, it is fired at 900 to 1,200 deg-C in an nitrogen atmosphere or nitrogen and hydrogen atmosphere, and the produced particles are again pulverized. Thereafter, the produced particles are annealed at 500 to 900 deg-C in an oxygen atmosphere or oxygen and nitrogen atmosphere in order to remove oxygen defects and to reduce their surfaces that adsorb water and hydrocarbon gases. The green phosphor which is charged positive is hence produced.

Description is provided next of the red phosphor of $(Y, Gd)_{1-x} BO_3:Eu_x$.

In the process of making a mixed solution, raw materials of yttrium nitrate, $Y_2(NO_3)_3$, gadolinium nitrate, $Gd_2(NO_3)_3$, boric acid, H_3BO_3, and europium nitrate, $Eu_2(NO_3)_3$ are mixed to a mole ratio of 1−X:2:X (where $0.05 \leq X \leq 0.20$). In this instance here, amounts of Y and Gd are arranged to a ratio of 65:35. The mixed materials are then fired at 1,200 to 1,350 deg-C for 2 hours in an air ambient, and classified to obtain the red phosphor. Since the red phosphor is fired in the air ambient, it contains comparatively small number of oxygen defects even if it is not annealed in an oxygen and nitrogen atmosphere. However, it is desirable to anneal it again because defects may develop in the process of classification.

Description is given next of the red phosphor of $Y_{2-x} O_3:Eu_x$.

In the process of making a mixed solution, raw materials of yttrium nitrate, $Y_2(NO_3)_3$, and europium nitrate, $Eu_2(NO_3)_3$ are mixed and dissolved into ion exchanged water to make a mole ratio of 2−X:X (where $0.05 \leq X \leq 0.30$). Subsequently, in the process of hydration, a basic aqueous solution such as ammonia solution is added to this mixed solution to produce a hydrate. Thereafter, in the process of hydrothermal synthesis, the hydrate is poured

together with ion exchanged water into a container made of a non-corrosive heat resistant material such as platinum or gold, and subjected to the hydrothermal synthesis for 3 to 12 hours under a temperature of 100 to 300 deg-C and a pressure of 0.2 to 10MPa in a pressurized vessel by using an autoclave, for instance. A resultant chemical compound is dried thereafter to obtain the desired phosphor particles of $Y_{2-x} O_3{:}Eu_x$.

Next, this phosphor is annealed at 1,300 to 1,400 deg-C for 2 hours in the air ambient, and classified to complete the red phosphor. The phosphor obtained by this process of hydrothermal synthesis has particles of approximately 0.1 to 2.0μm in diameter, and they become spherical in shape. These particle diameters and shapes are suitable to form a phosphor layer of outstanding light emitting property. The above red phosphors do not have many oxygen defects since they are fired in the air ambient, and amounts of adsorption of water and hydrocarbon gases are therefore very limited.

As described above, green phosphors used in this invention are the spinel group phosphors such as $Zn(Ga_{1-x}Al_x)_2 O_4{:}Mn$, $Mg(Ga_{1-x}Al_x)_2 O_4{:}Mn$, $Ca(Ga_{1-x}Al_x)_2 O_4{:}Mn$ and $Sr(Ga_{1-x}Al_x)_2 O_4{:}Mn$, of which surfaces are charged positive (+). Also used are green phosphors containing yttria such as $(Y_{1-x}Gd_x) BO_3{:}Tb$, $(Y_{1-x}Gd_x) Al_3 (BO_3)_4{:}Tb$, $(Y_{1-x}Gd_x) Al_3 (BO_3)_4{:}Tb$, $(Y_{1-x}Gd_x) Al_3 (BO_3)_4{:}Ce$ and $Y_3 Al_3 Ga_2 O_{12}{:}Tb$, all having their surfaces charged positive (+)

The conventional green phosphor of $Zn_2 Si O_4{:}Mn$ tends to clog the nozzle in the phosphor forming process, and it is liable to decrease brightness when the green color is lit, since it is charged negative. However, the green phosphors according to this invention, when used, obviate clogging of the nozzle during the process of depositing the phosphors, eliminate color blur and degradation in the brightness of the panel as well as failures of address discharge, and they can hence improve brightness of the full-on white display.

PDP provided with the phosphors of this invention were assembled in plasma display devices, and their performances were evaluated as detailed below. A number of phosphor samples were prepared according to the above exemplary embodiment, the PDP produced by using these samples were then assembled in the plasma display devices, and they were tested for this performance evaluation.

The individual plasma display devices produced here have a screen size of 42 inches (i.e., HD-TV specifications having rib pitches of 150μm), dielectric glass layers of 20μm thick, MgO protective layers of 0.5μm thick, and intervals of 0.08mm between the display electrodes and the display scan electrodes. In addition, their discharge spaces are filled with discharge gases consisting primarily of neon gas mixed with xenon gas in a ratio between 5% and 90% at a pressure of 66.5kPa.

Table 1 is a list of combinations of the phosphor samples used for the individual PDP.

[Table 1]

Sample No.	Type and Combination of Green Phosphor	Type of Blue Phosphor	Type of Red Phosphor
1	$Zn_{1-a}(Ga_{1-x}Al_x)_2O_4:Mn_a$ a=0.01, x=0.5	$BaMgAl_{10}O_{17}:Eu$	$(Y,Gd)BO_3:Eu$
2	$Zn_{1-a}(Ga_{1-x}Al_x)_2O_4:Mn_a$ a=0.02, x=1.0	Same as above	Same as above
3	$Ca_{1-a}(Ga_{1-x}Al_x)_2O_4:Mn_a$ a=0.04, x=1.0	Same as above	Same as above
4	$Mg_{1-a}(Ga_{1-x}Al_x)_2O_4:Mn_a$ a=0.03, x=0.5	Same as above	Same as above
5	$Zn_{1-a}(Ga_{1-x}Al_x)_2O_4:Mn_a$ a=0.03, x=0.5	$(Ba,Sr)MgAl_{10}O_{17}:Eu$	$Y_2O_3:Eu$
6	$Sr_{1-a}(Ga_{1-x}Al_x)_2O_4:Mn_a$ a=0.03, x=1	Same as above	Same as above

7	Mixture of sample no. 1 and $(Y_{1-a-y}Gd_a)(Ga_{1-x}Al_x)_3(BO_3)_4$:$Tb_y$ a=0, x=0.1 and y=0.02 (mixing ratio of 45:55)	Same as above	Same as above
8	Mixture of sample no. 2 and $(Y_{1-a-y}Gd_a)(Ga_{1-x}Al_x)_3(BO_3)_4$:$Tb_y$ a=0.5, x=0.5 and y=0.3 (mixing ratio of 45:50)	Same as above	Same as above
9	Mixture of sample no. 3 and $(Y_{1-a-y}Gd_a)(Ga_{1-x}Al_x)_3(BO_3)_4$:$Ce_y$, Tb_y, a=0.9, x=1 and y=0.02 (mixing ratio of 50:50)	Same as above	Same as above
10	Mixture of sample no. 4 and $(Y_{1-a-y}Gd_a)(Ga_{1-x}Al_x)_3(BO_3)_4$:$Tb_y$ a=0, x=1 and y=0.4 (mixing ratio of 40:60)	Same as above	Same as above
11	Mixture of sample no. 5 and $(Y_{1-a-y}Gd_a)(Ga_{1-x}Al_x)_3(BO_3)_4$:$Tb_y$ a=0.5, x=0.8 and y=0.1 (mixing ratio of 40:60)	Same as above	Same as above
12	Mixture of sample no. 6 and $(Y_{1-a-y}Gd_a)_3(Ga_{1-x}Al_x)_5O_{12}$:$Tb_y$ a=0.5, x=1 and y=0.03 (mixing ratio of 30:60)	$BaMgAl_{10}O_{17}$:Eu	(Y, Gd)BO_3:Eu
13	Mixture of sample no. 4 and $(Y_{1-a-y}Gd_a)BO_3$:Tb_y a=0.5 and y=0.03 (mixing ratio of 40:60)	Same as above	Same as above
14*	Mixture of Zn_2SiO_4:Mn and $(Y_{1-a-y}Gd_a)(Ga_{1-x}Al_x)_3BO_3$:$Tb_y$ a=0.5, x=1 and y=0.03 (mixing ratio of 50:50)	Same as above	Same as above
15*	Mixture of $BaAl_{12}O_{19}$:Mn and $(Y_{1-a-y}Gd_a)(Ga_{1-x}Al_x)_3BO_3$:Tb a=0.5, x=1 and y=0.03 (mixing ratio of 50:50)	Same as above	Same as above
16*	Zn_2SiO_4:Mn	Same as above	Same as above
17*	$BaMgAl_{14}O_{23}$:Mn, Eu	Same as above	Same as above
18*	$BaAl_{12}O_{19}$:Mn	Same as above	Same as above
19*	Mixture of $BaAl_{12}O_{19}$:Mn and $LaPO_4$:Tb (mixing ratio of 50:50)	Same as above	Same as above

* Sample numbers 14 to 19 are reference samples for comparison.

Phosphor particles used for samples 1 to 6 are a variety of spinel group compounds M_{1-a} $(Ga_{1-x}Al_x)_2$ O_4:Mn_a (where M represents one of Zn, Mg, Ca and Sr) as the green phosphors which are charged positive, BaMg $Al_{10}O_{17}$:Eu as the blue phosphors, and (Y,Gd) BO_3:Eu as the red phosphors. In addition, Table 1 shows values of "a" and "x", and kinds of the M element.

Phosphor particles used as the green phosphors of samples 7 to 13 are a variety of mixed combinations between one of the spinel group compounds M_{1-a} $(Ga_{1-x}Al_x)_2$ O_4:Mn_a (where M represents one of Zn, Mg, Ca and Sr) and one of yttria group compounds $(Y_{1-b-y}Gd_b)$ $(Ga_{1-x}Al_x)_3$ $(BO_3)_4$:Tb_y, $(Y_{1-b-y}Gd_b)$ $(Ga_{1-x}Al_x)_3$ $(BO_3)_4$:Tb_y, $(Y_{1-b-y}Gd_b)$ $(Ga_{1-x}Al_x)_3$ $(BO_3)_4$:Ce_y, $(Y_{1-a-y}Gd_a)_3$ $(Ga_{1-x}Al_x)_5$ O_{12}:Tb_y and $(Y_{1-b-y}Gd_b)$ BO_3:Tb_y, which are charged positive. Also, phosphor particles used are BaSr Mg $Al_{10}O_{17}$:Eu as the blue phosphors, and Y_2O_3:Eu as the red phosphors. Table 1 shows individual values of "a", "x", "b" and "y", and kinds of the M element.

The green phosphors of samples 14 to 19 for the comparison purpose are phosphor materials, each containing any one of Zn_2SiO_4:Mn, Ba $Al_{12}O_{17}$:Mn, Ba Mg $Al_{14}O_{23}$:Eu, Mn and $LaPO_4$:Tb. These samples also use Ba Sr $Al_{10}O_{17}$:Eu as the blue phosphor, and Y_2O_3:Eu as the red phosphor. Table 1 shows compositions of the individual phosphors.

The following experiments were conducted on those samples.

(Experiment 1)

Amounts of electric charges were measured on the green phosphors of the produced samples 1 through 13 and the reference samples 14 through 19 by using a blow-off method, which can check the amounts of charges on reduced iron powder. The measurements were taken according to a method introduced in Journal of The Illuminating Engineering Institute of Japan, Vol. 76, No. 10,

published in 1992, PP 16 – 27. As a result, it became clear that all of the samples carry positive charges, except for the samples 14 and 16 which contain Zn_2SiO_4:Mn, and they therefore carry negative charges.

(Experiment 2)

The phosphors (i.e., blue, green and red colors) in the produced panels were taken out, and amounts of adsorbed water, CO, CO_2 and hydrocarbon were measured by the TDS (i.e., Temperature-programmed desorption gaseity amount analysis method). For the test specimens, 100mg each of the phosphors were taken from inside of the produced panels, they were heated from the room temperature to 600 deg-C, and gross weights of escaped water and hydrocarbon group gases were measured. At the same time, amounts of the water and hydrocarbon group gases of the samples 2 to 19 were compared in relation to amounts of the water and hydrocarbon group gases of the sample 1, which were reckoned at 1 and used as the base values.

(Experiment 3)

Brightness (in full-on white, green, blue and red colors) and color temperatures of the panels were measured by using a luminance meter right after completion of the manufacturing process.

(Experiment 4)

In the measurements of degradation in the brightness and color temperatures of the panels when lit to the full-on white screen, the PDP were impressed continuously with discharge sustaining pulses of 175V and 200kHz in voltage and frequency for 500 hours, and the brightness and color temperatures were measured before and after the operation. Rates of change in brightness degradation (i.e., [(brightness after the operation – brightness before the operation) / brightness before the operation] x 100) and rates of change in color temperatures were obtained from the above results. In determining address

error during address discharges, display images were examined for presence or absence of flickers, and an error was determined exist even when there was only one.

Table 2 shows results of the above experiments 1 through 4 on the rates of change in the brightness degradation of the green color as well as the full-on white screen, and also presence and absence of the address error.

[Table 2]

Sample No.	Ratio of water & hydrocarbon adsorbed in phosphors (in 100mg) as compared to basic sample no. 1		Rate of change in brightness of panel (%), after 1000 hours of sustaining discharge in full-white screen with 185V, 200kHz				Rate of change in brightness of green color (%), after 1000 hour application of discharge sustaining pulses of 185V, 200kHz				Presence of address error in address discharge and clogging of nozzle			
	Water	Hydrocarbon	Xe 5%	Xe 10%	Xe 20%	Xe 60%	Xe 5%	Xe 10%	Xe 20%	Xe 60%	Xe 5%	Xe 10%	Xe 20%	Xe 60%
1	1	1	-2.5	-2.4	-2.4	-2.2	-2.3	-2.2	-2.1	-2	none	none	none	none
2	1.1	1.3	-2.9	-2.7	-2.5	-2.3	-2.7	-2.5	-2.3	-2.1	none	none	none	none
3	1.2	1.2	-3	-2.9	-2.7	-2.6	-2.9	-2.5	-2.1	-1.9	none	none	none	none
4	1.1	1.2	-3.1	-3	-2.8	-2.5	-3	-2.7	-2.4	-1.6	none	none	none	none
5	0.9	0.8	-2.3	-2.3	-2.5	-2.2	-2.2	-2.1	-2.4	-1.8	none	none	none	none
6	1.1	1	-2.6	-2.5	-2.5	-2.3	-2.4	-2.3	-2.3	-2.0	none	none	none	none
7	0.8	0.7	-2.2	-2.4	-2.1	-2	-2	-2.2	-2	-1.7	none	none	none	none
8	0.6	0.7	-2	-1.9	-1.8	-1.5	-1.8	-1.6	-1.5	-1.2	none	none	none	none
9	0.7	0.5	-2.1	-2	-2	-1.8	-1.9	-1.7	-1.7	-1.5	none	none	none	none
10	0.6	0.6	-1.9	-1.8	-1.6	-1.5	-1.6	-1.5	-1.3	-1.0	none	none	none	none
11	0.7	0.8	-2.2	-2	-2.1	-1.8	-1.9	-1.7	-1.8	-1.6	none	none	none	none
12	0.7	0.6	-2.2	-1.9	-1.8	-1.6	-1.8	-1.7	-1.6	-1.1	none	none	none	none
13	0.5	0.6	-1.5	-1.6	-1.4	-1.3	-1.2	-1.3	-1.2	-1	none	none	none	none
14*	2.4	2.6	-4.1	-4	-3.8	-3.5	-4	-2.8	-3.5	-3.3	yes	yes	yes	yes
15*	2.4	2.6	-4.6	-4.5	-4.3	-4.1	-4.3	-4.2	-4.1	-3.9	none	none	none	none
16*	2.5	2.6	-4.8	-4.6	-4.7	-4.5	-4.5	-4.3	-4.6	-4.2	yes	none	none	none
17*	3.2	3.4	-5.4	-5.3	-5.3	-5.2	-5.2	-5	-5.1	-5.1	none	none	none	none
18*	4.2	4.1	-5.9	-5.6	-5.5	-5.1	-5.5	-5.2	-5	-5	none	none	none	none
19*	4	4.2	-5.1	-5.2	-5.3	-5	-4.9	-5	-5.1	-4.8	none	none	none	none

*Sample numbers 14 to 19 are reference samples for comparison.

As shown in Table 2, the green phosphors provided in the reference samples 14 through 19 are a mixture of Zn_2SiO_4:Mn and (Y, Gd) BO_3:Tb for the sample 14, a mixture of Ba $Al_{12}O_{19}$:Mn and (Y, Gd)BO_3 for the sample 15, Zn_2SiO_4:Mn for the sample 16, Ba Mg $Al_{14}O_{23}$:Eu, Mn for the sample 17, Ba $Al_{12}O_{19}$:Mn for the sample 18, and a mixture of $BaAl_{12}O_{17}$:Mn and $LaPO_4$:Tb for the sample 19, and the blue phosphors provided are Ba Sr Mg $Al_{10}O_{17}$:Eu for all of them. Therefore, large amounts of water and hydrocarbon group gases were adsorbed by these phosphors. The amounts of adsorbed water, in particular, were 2 to 5 times as large as compared to those of the embodied samples of this invention. The amounts of hydrocarbon group gases were also larger by 2 to 5 times, although absolute amounts of them are 1/5 to 1/10 of the water.

For this reason, the reference samples 14 to 19 showed substantial decrease in brightness of the green and blue colors during the discharging operation, and many address errors were recorded especially when the partial pressure of Xe gas exceeds 10%. Since samples 16 and 18, in particular, use the green phosphors of single component, such as Zn_2SiO_4:Mn and $BaAl_{12}O_{19}$, they adsorbed large amounts of water and hydrocarbon group gases, and exhibited especially large numbers of address errors and substantial degradation in the brightness attributable to the ultraviolet rays (in 147nm) and the discharge sustaining pulses.

To this contrary, all of the panels having the green, blue and red color combinations of samples 1 to 13 showed only small degrees of change in the brightness of the individual colors attributable to the ultraviolet rays (in 147nm) and the discharge sustaining pulses, and they did not exhibit any reduction in the color temperature, address errors, and clogging of the nozzle in the process of depositing the phosphors. This is because they use the green phosphors made of any one or a mixed combination of $M_{1-a}(Ga_{1-x}Al_x)_2O_4$:Mn of

the spinel crystal structure containing aluminum, and $(Y_{1-b-y}Gd_b)$ $(Ga_{1-x}Al_x)_3$ $(BO_3)_4$:Tb_y, $(Y_{1-b-y}Gd_a)$ $(Ga_{1-x}Al_x)_3$ $(BO_3)_4$:Ce_y, Tb_y, $(Y_{1-a-y}Gd_y)_3$ $(Ga_{1-x}Al_x)_5$ O_{12}:Tb_y and $(Y_{1-b-y}Gd_b)$ BO_3:Tb_y, all containing yttrium, instead of the conventional green phosphors which are liable to adsorb water and hydrocarbon, thereby restricting release of the water and hydrocarbon inside the panels, and preventing degradation in the brightness due to the discharge and address errors attributable to the deterioration of MgO.

INDUSTRIAL APPLICABILITY

According to the present invention as described above, the phosphor crystals of the individual colors are composed of such compounds that carry positive charges. In particular, the green phosphor layers are formed of the spinel group and the yttria group phosphor particles having the base elements of aluminum and yttrium which do not adsorb large amounts of moisture and hydrocarbon. The invention can hence provide the highly reliable panel with small degradation in the brightness and color temperature without causing address errors even when a partial pressure of the Xe gas inside the panel rises, and it is therefore useful for a display device of large screen.